

Form PTO-1390  
(Rev. 12-29-99)

US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NO.

H 3294 PCT/US

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (If known, enter)

097869171

INTERNATIONAL APPLICATION NO.  
**PCT/EP99/09901**

INTERNATIONAL FILING DATE  
**December 14, 1999**

PRIORITY DATE CLAIMED  
**December 23, 1998**

**TITLE OF INVENTION**

**AGENT FOR COLORING KERATINACEOUS FIBERS**

**APPLICANT(S) FOR DO/EO/US**

**Horst Hoeffkes, Doris Oberkobusch, David Rose, Melanie Hitz**

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
  2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
  3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
  4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
  5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
    - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☒ has been transmitted by the International Bureau.
    - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
  6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
  7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
    - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau)
    - b. ☐ have been transmitted by the International Bureau.
    - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
    - d. ☒ have not been made and will not be made.
  8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
  9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). UNEXECUTED
  10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. ☒ A **FIRST** preliminary amendment
  - ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
  14. ☐ A substitute specification.
  15. ☐ A change of power of attorney and/or address letter.
  16. ☒ Other items or information:

PTO Form 1449 (with references)

"Express Mail" mailing label number E615775777US

25 JUN 2001

U.S. Application No. (if known, see 37 CFR 1.5) <u>09/869171</u>	INTERNATIONAL APPLICATION NO. PCT/EP99/09901	ATTORNEY'S DOCKET NUMBER H 3294 PCT/US
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17. The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... <b>\$1000.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO..... <b>\$860.00</b>  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$710.00</b>  International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$690.00</b>  International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)..... <b>\$100.00</b>	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="text-align: left;">CALCULATIONS</th> <th style="text-align: left;">PTO USE ONLY</th> </tr> <tr> <td style="height: 100px; vertical-align: top;"> <div style="text-align: right; margin-bottom: 10px;"><b>ENTER APPROPRIATE BASIC FEE AMOUNT</b></div> <div style="text-align: right;">Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%;">CLAIMS</th> <th style="width: 20%;">NUMBER FILED</th> <th style="width: 20%;">NUMBER EXTRA</th> <th style="width: 20%;">RATE</th> <th style="width: 20%;"></th> </tr> <tr> <td>Total Claims</td> <td>1 - 20 =</td> <td>0</td> <td>0 X \$18.00</td> <td>\$ 0</td> </tr> <tr> <td>Independent Claims</td> <td>1 - 3 =</td> <td>0</td> <td>0 X \$80.00</td> <td>\$ 0</td> </tr> <tr> <td colspan="4">Multiple dependent claims (s) (if applicable)</td> <td>0 + \$270.00</td> </tr> <tr> <td colspan="4"><b>TOTAL OF ABOVE CALCULATIONS</b></td> <td><b>\$ 860</b></td> </tr> <tr> <td colspan="4">Reduction of 1/2 for filing by small entity, if applicable. 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A duplicate copy of this sheet is enclosed.</p> <p><b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b))    must be filed and granted to restore the application to pending status.</b></p> <p>SEND ALL CORRESPONDENCE TO: Henkel Corporation, Law Dept.    2500 Renaissance Blvd., Suite 200    Gulph Mills, PA 19406</p> <p style="text-align: right;"> <i>Kimberly R. Hild</i>      SIGNATURE: _____       Kimberly R. Hild      NAME ATTORNEY FOR APPLICANT      39,224      REGISTRATION NUMBER   </p>	CALCULATIONS	PTO USE ONLY	<div style="text-align: right; margin-bottom: 10px;"><b>ENTER APPROPRIATE BASIC FEE AMOUNT</b></div> <div style="text-align: right;">Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).</div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%;">CLAIMS</th> <th style="width: 20%;">NUMBER FILED</th> <th style="width: 20%;">NUMBER EXTRA</th> <th style="width: 20%;">RATE</th> <th style="width: 20%;"></th> </tr> <tr> <td>Total Claims</td> <td>1 - 20 =</td> <td>0</td> <td>0 X \$18.00</td> <td>\$ 0</td> </tr> <tr> <td>Independent Claims</td> <td>1 - 3 =</td> <td>0</td> <td>0 X \$80.00</td> <td>\$ 0</td> </tr> <tr> <td colspan="4">Multiple dependent claims (s) (if applicable)</td> <td>0 + \$270.00</td> </tr> <tr> <td colspan="4"><b>TOTAL OF ABOVE CALCULATIONS</b></td> <td><b>\$ 860</b></td> </tr> <tr> <td colspan="4">Reduction of 1/2 for filing by small entity, if applicable. 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09/869171

JC03 Rec'd PCT/TTL 25 JUN 2001

PATENT  
Docket No. H 3294 PCT/US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**In re Application of:**  
Hoeffkes, et al.

**International Application No.** PCT/EP99/09901  
**International Filing Date:** December 14, 1999

**Serial No.** To be assigned **Examiner:** To be assigned  
**Filed:** To be assigned **Art Unit:** To be assigned

**Title:** AGENT FOR COLORING KERATINACEOUS FIBERS

"Express Mail Post Office to Addressee" service mailing label number EL615775777US

**PRELIMINARY AMENDMENT**

Box PCT  
Assistant Commissioner for Patents  
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

**In the Specification (Using the English Translation):**

On page 1 of the English translation, on a separate line between the title and line 1, please insert the following header and paragraph on consecutive lines as shown below:

**-- CROSS REFERENCE TO RELATED APPLICATIONS**

This application is a national stage application under 35 U.S.C. § 371 of international application PCT/EP99/09901 filed on December 14, 1999, the international

09869171-103101

**Docket No. H3294 PCT/US  
PCT/EP99/09901**

application not being published in English. This application also claims priority under 35 U.S.C. §119 to DE 198 59 800.9, filed on December 23, 1998. --

On page 1, on a separate line immediately after the above inserted paragraph and before line 1, please insert the following header:

-- FIELD OF THE INVENTION --.

On page 1, on a separate line between lines 6 and 7, please insert the following header:

-- BACKGROUND OF THE INVENTION -- .

On page 3, on a separate line between lines 16 and 17, please insert the following header:

-- SUMMARY OF THE INVENTION --.

On page 7, on a separate line between lines 19 and 20, please insert the following header:

-- DETAILED DESCRIPTION OF THE INVENTION --.

On page 26, line 1, please replace the heading "Patent claims" with the following heading:

-- What is claimed is: --

On a separate page, after page 40, please insert the enclosed Abstract of the Disclosure.

**In the Claims**

Please cancel Claims 2 to 13, without prejudice.

**REMARKS**

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

**Status of Claims**

Claim 1 will be pending after entry of the present amendment. Claims 2 to 13 are being canceled without prejudice.

**Amendment**

The specification is being amended to insert section headers and an abstract of the disclosure in accordance with 37 CFR §1.77 to better conform with US patent practice. The specification is also being amended to insert a cross-reference to related applications in accordance with 37 CFR §1.78 and to claim priority to those applications listed therein.

Applicants submit herewith "Version With Markings To Show Changes Made" to show the amendments made to the specification.

## CONCLUSION

The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,

Kimberly R. Abild

Kimberly R. Hild  
(Reg. No. 39,224)  
Attorney for Applicants  
(610) 278-4964

Henkel Corporation  
Law Department  
2500 Renaissance Boulevard, Suite 200  
Gulph Mills, PA 19406

**Abstract of the Disclosure**

The present invention relates to a composition for coloring keratinaceous fibers and a method of using the same. The composition of the present invention contains (a) at least one pyrimidine derivative and (b) at least one compound selected from an m-phenylene derivative, an m-aminophenol derivative, a pyridine derivative, a resorcinol derivative, a methylenedioxybenzene derivative, or 3,4-diaminobenzoic acid or combinations thereof. The method of the present invention includes applying the coloring composition to keratin-containing fibers and subsequently rinsing the coloring composition from the fibers.

PATENT  
Docket No. H 3294 PCT/US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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Hoeffkes, et al.

**International Application No.** PCT/EP99/09901  
**International Filing Date:** December 14, 1999

**Serial No.** 09/869,171 **Examiner:** To be assigned  
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**Title:** AGENT FOR COLORING KERATINACEOUS FIBERS

"Express Mail Post Office to Addressee" service mailing label number EL615775485US

**SUPPLEMENTAL PRELIMINARY AMENDMENT**

Box PCT  
Assistant Commissioner for Patents  
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

**In the Specification**

Please replace the paragraph on page 23, lines 2 to 4 with the following new paragraph:

-- Hair dyeing agents according to the invention were in the form of a hair dyeing cream emulsion of the composition given in Table 1. --

**In the Claims**

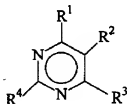
Please cancel Claim 1, without prejudice.

09869171-103101



Please add the following new claims:

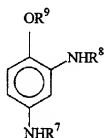
14. (NEW) A method of coloring keratin fibers comprising  
(A) applying to keratin fibers a coloring composition formed from components comprising  
(a) at least one pyrimidine derivative of formula I



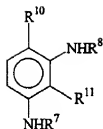
(I)

wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are, independently of one another, selected from hydrogen, an OH group, a NH<sub>2</sub> group, or a NR<sup>5</sup>R<sup>6</sup> group, wherein R<sup>5</sup> and R<sup>6</sup> are independently selected from a C<sub>1</sub> to C<sub>4</sub> alkyl group, or a C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl group having one or more hydroxyl groups that are primary, secondary or combinations thereof, or where two of the R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> substituents together form a 5 or 6 member, optionally substituted, heterocycle ring containing one or two nitrogen atoms, or one or two oxygen atoms or a combination of both in the heterocycle ring, with the proviso that at least two of the R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> substituents are a NH<sub>2</sub> group or NR<sup>5</sup>R<sup>6</sup> group, and

- (b) at least one compound selected from  
(i) m-phenylene derivatives of formula II or III

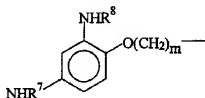


(II)



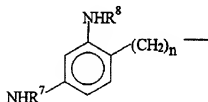
(III)

wherein  $R^7$ ,  $R^8$  and  $R^{11}$  are independently from one another hydrogen, a  $C_1$  to  $C_4$  alkyl group or a  $C_1$  to  $C_4$  hydroxyalkyl group,  $R^9$  is a  $C_1$  to  $C_4$  hydroxyalkyl group or a radical of formula IV



(IV)

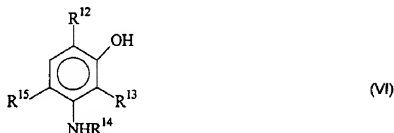
in which  $R^7$  and  $R^8$  are defined as above and  $m$  is an integer from 1 to 4, and  $R^{10}$  is hydrogen or a radical of formula V



(V)

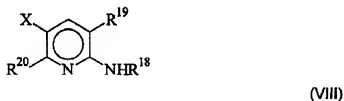
in which  $R^7$  and  $R^8$  are as defined above and  $n$  is an integer from 1 to 4,

(ii) m-aminophenol derivatives of formula (VI)



wherein  $R^{12}$  is hydrogen or a  $C_1$  to  $C_4$  alkyl group,  $R^{13}$  is hydrogen, fluorine, chlorine, an  $OCH_3$  group or a  $C_1$  to  $C_4$  alkyl group,  $R^{14}$  is hydrogen, a  $C_1$  to  $C_4$  alkyl group, a  $C_1$  to  $C_4$  hydroxyalkyl group or an  $OCF_3$  group,  $R^{15}$  is hydrogen, fluorine, chlorine or an  $OCH_3$  group, with the provisos that  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  are not hydrogen at the same time, and that, if  $R^{12}$  is methyl,  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  are not hydrogen at the same time,

(iii) pyridine derivatives of formula VII or VIII



wherein  $R^{16}$  and  $R^{17}$  are independently fluorine, chlorine or an  $OCH_3$  group,  $R^{18}$  is hydrogen, a  $C_1$  to  $C_4$  alkyl group or a  $C_1$  to  $C_4$  hydroxyalkyl group,  $R^{19}$  is an  $OH$  group or  $NH_2$  group,  $R^{20}$  is hydrogen, a  $C_1$  to  $C_4$  alkoxy group or a  $NH_2$  group,  $X$  is hydrogen or

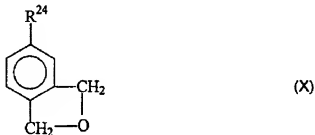
an OCH<sub>3</sub> group, with the provisos that, if R<sup>19</sup> is NH<sub>2</sub>, R<sup>18</sup> and R<sup>20</sup> are not a C<sub>1</sub> to C<sub>4</sub> alkyl group and a methoxy group, respectively, at the same time, and if R<sup>18</sup> is hydrogen, R<sup>19</sup> and R<sup>20</sup> are not an OH group and hydrogen, respectively, at the same time,

(iv) resorcinol derivatives of formula IX



wherein R<sup>21</sup>, R<sup>22</sup> and R<sup>23</sup> are independently from one another hydrogen, a C<sub>1</sub> to C<sub>4</sub> alkyl group or a C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl group, with the provisos that R<sup>21</sup>, R<sup>22</sup> and R<sup>23</sup> are not hydrogen at the same time, R<sup>22</sup> is not methyl if R<sup>21</sup> and R<sup>23</sup> are hydrogen, and R<sup>22</sup> and R<sup>23</sup> are not hydrogen at the same time if R<sup>21</sup> is methyl,

(v) methylenedioxybenzene derivatives of formula X



wherein R<sup>24</sup> is an OH group, a NH<sub>2</sub> group or a NHR<sup>25</sup> group, in which R<sup>25</sup> is a C<sub>1</sub> to C<sub>4</sub> alkyl group or a C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl, or

(vi) 3,4-diaminobenzoic acid, or

(vii) combinations thereof; and

(B) oxidatively developing the coloring composition using atmospheric oxygen, an enzyme containing system, or combinations thereof as the sole oxidizing agent.

15. (NEW) The method of claim 14 wherein the pyrimidine derivative is 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-2,5,6-triaminopyrimidine, 2,4,5,6-tetraaminopyrimidine, 5,6-diamino-2,4-dihydroxypyrimidine, 2,4-diamino-5,6-dihydroxypyrimidine, or 4-methylamino-2,5,6-tetraminopyrimidine, or combinations thereof.

16. (NEW) The method of claim 15 wherein the pyrimidine derivative is 2,4,5,6-tetraaminopyrimidine.

17. (NEW) The method of claim 15 wherein the pyrimidine derivative is present in the coloring composition in an amount of from 0.03 mmol to 65 mmol, based on 100 g of the coloring composition as a whole.

18. (NEW) The method of claim 14 wherein at least one of  $R^7$  and  $R^8$  of the Formula III is a  $C_1$  to  $C_4$  alkyl group or a  $C_1$  to  $C_4$  hydroxyalkyl group, and wherein  $R^{20}$  of the Formula VIII is hydrogen or a  $C_1$  to  $C_4$  alkoxy group.

19. (NEW) The method of claim 14 wherein the component B comprises 1,3-bis(2,4-diaminophenoxy)propane, 1,3-bis(2,4-diaminophenyl)propane, 2,4-diaminophenoxyethanol, 2,6-bis(2'-hydroxyethylamino)toluene, 3-amino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 2,4-dichloro-3-aminophenol, 3,5-diamino-2,6-dimethoxypyridine, 5-methylresorcinol, 2,5-dimethylresorcinol, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline, or N-(2-hydroxyethyl)-3,4-methylenedioxyaniline, or combinations thereof.

20. (NEW) The method of claim 19 wherein each compound of component B is present in the coloring composition in an amount of 0.03 mmol to 65 mmol, based on 100 g of the coloring composition as a whole.

21. (NEW) The method of claim 14 wherein the coloring composition further comprises at least one activated carbonyl compound selected from the group consisting of isatin, 5-chloroisatin, 5-bromoisatin, 6-bromoisatin, 5-nitroisatin, N-hydroxymethylisatin, N-allylisatin, 5-isatinsulfonic acid Na salt, glutaconaldehyde tetrabutylammonium salt, tribase aldehyde, malonaldehyde bis(dimethyl acetal), 4-hydroxy-3-methoxycinnanaldehyde, 1-piperidino-methylisatin, 1-diethylaminomethylisatin, glutaconaldehyde Na salt, 5-N-methylanilinopentadienyl, 2-chloro-3-hydroxymethylene-1-cyclohexene 1-aldehyde, N-(5-anilino-2,4-pentadien-1-ylidene)anilinium chloride, trans- $\beta$ -(2-furyl)acrolein, 2-nitro-1,3-indanedione, dehydroascorbic acid, 2-acetyl-1,3-cyclohexanedione, 7-dimethylamino-2,4,6-heptatrienyliidene dimethylammonium perchlorate, 4-formyl-1-methylpyridinium benzenesulfonate, and combinations thereof.

22. (NEW) The method of claim 14 wherein the coloring composition further comprises one or more compounds selected from 5,6-dihydroxyindole or its N-substituted C<sub>1</sub> to C<sub>4</sub> alkyl or C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl derivatives, or 5,6-dihydroxyindoline or its N-substituted C<sub>1</sub> to C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl derivatives or combinations thereof.

23. (NEW) The method of claim 14 wherein the coloring composition further comprises one or more compounds selected from p-phenylenediamine, p-tolylenediamine, p-aminophenol, 4,4'-diaminodiphenylamine, 1,10-bis(2,5-diaminophenyl)-1,4,7,10-tetraoxydecane, 2,(2'-hydroxyethyl)-p-phenylenediamine, 2,6-dichloro-4-aminophenol, N,N-bis(2'-hydroxyethyl)-p-phenylenediamine, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 5-aminosalicylic acid, bis(2-hydroxy-5-aminophenyl)methane, or 2-(2,5-diaminophenoxy)ethanol, or combinations thereof.

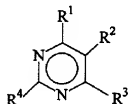
24. (NEW) The method of claim 14 wherein the coloring composition further comprises anionic surfactants, zwitterionic surfactants, nonionic surfactants, or combinations thereof.

25. (NEW) The method of claim 14 wherein the coloring composition is combined with an enzyme containing system before the application of the coloring composition to the keratin fibers.

26. (NEW) A method of coloring keratin fibers comprising

(A) applying to keratin fibers

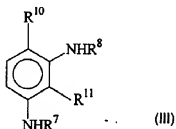
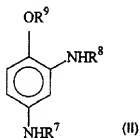
(a) at least one pyrimidine derivative of formula I



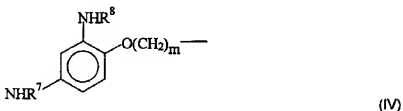
(I)

wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are, independently of one another, selected from hydrogen, an OH group, a NH<sub>2</sub> group, or a NR<sup>5</sup>R<sup>6</sup> group, wherein R<sup>5</sup> and R<sup>6</sup> are independently selected from a C<sub>1</sub> to C<sub>4</sub> alkyl group, or a C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl group having one or more hydroxyl groups that are primary, secondary or combinations thereof, or where two of the R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> substituents together form a 5 or 6 member, optionally substituted, heterocycle ring containing one or two nitrogen atoms, or one or two oxygen atoms or a combination of both in the heterocycle ring, with the proviso that at least two of the R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> substituents are a NH<sub>2</sub> group or NR<sup>5</sup>R<sup>6</sup> group; and

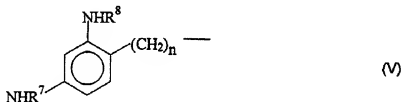
- (b) at least one compound selected from  
 (i) m-phenylene derivatives of formula II or III



wherein  $R^7$ ,  $R^8$  and  $R^{11}$  are independently from one another hydrogen, a  $C_1$  to  $C_4$  alkyl group or a  $C_1$  to  $C_4$  hydroxyalkyl group,  $R^9$  is a  $C_1$  to  $C_4$  hydroxyalkyl group or a radical of formula IV



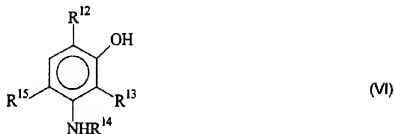
in which  $R^7$  and  $R^8$  are defined as above and  $m$  is an integer from 1 to 4, and  $R^{10}$  is hydrogen or a radical of formula V



in which  $R^7$  and  $R^8$  are as defined above and  $n$  is an integer from 1 to 4,

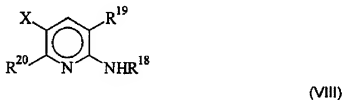
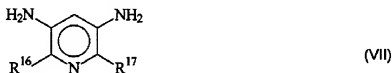


(ii) m-aminophenol derivatives of formula (VI)



wherein R<sup>12</sup> is hydrogen or a C<sub>1</sub> to C<sub>4</sub> alkyl group, R<sup>13</sup> is hydrogen, fluorine, chlorine, an OCH<sub>3</sub> group or a C<sub>1</sub> to C<sub>4</sub> alkyl group, R<sup>14</sup> is hydrogen, a C<sub>1</sub> to C<sub>4</sub> alkyl group, a C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl group or an OCF<sub>3</sub> group, R<sup>15</sup> is hydrogen, fluorine, chlorine or an OCH<sub>3</sub> group, with the provisos that R<sup>12</sup>, R<sup>13</sup>, R<sup>14</sup> and R<sup>15</sup> are not hydrogen at the same time, and that, if R<sup>12</sup> is methyl, R<sup>13</sup>, R<sup>14</sup> and R<sup>15</sup> are not hydrogen at the same time,

(iii) pyridine derivatives of formula VII or VIII



wherein R<sup>16</sup> and R<sup>17</sup> are independently fluorine, chlorine or an OCH<sub>3</sub> group, R<sup>18</sup> is hydrogen, a C<sub>1</sub> to C<sub>4</sub> alkyl group or a C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl group, R<sup>19</sup> is an OH group or NH<sub>2</sub> group, R<sup>20</sup> is hydrogen, a C<sub>1</sub> to C<sub>4</sub> alkoxy group or a NH<sub>2</sub> group, X is hydrogen or

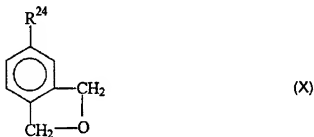
an  $\text{OCH}_3$  group, with the provisos that, if  $\text{R}^{19}$  is  $\text{NH}_2$ ,  $\text{R}^{18}$  and  $\text{R}^{20}$  are not a  $\text{C}_1$  to  $\text{C}_4$  alkyl group and a methoxy group, respectively, at the same time, and if  $\text{R}^{18}$  is hydrogen,  $\text{R}^{19}$  and  $\text{R}^{20}$  are not an OH group and hydrogen, respectively, at the same time,

(iv) resorcinol derivatives of formula IX



wherein  $\text{R}^{21}$ ,  $\text{R}^{22}$  and  $\text{R}^{23}$  are independently from one another hydrogen, a  $\text{C}_1$  to  $\text{C}_4$  alkyl group or a  $\text{C}_1$  to  $\text{C}_4$  hydroxyalkyl group, with the provisos that  $\text{R}^{21}$ ,  $\text{R}^{22}$  and  $\text{R}^{23}$  are not hydrogen at the same time,  $\text{R}^{22}$  is not methyl if  $\text{R}^{21}$  and  $\text{R}^{23}$  are hydrogen, and  $\text{R}^{22}$  and  $\text{R}^{23}$  are not hydrogen at the same time if  $\text{R}^{21}$  is methyl,

(v) methylenedioxybenzene derivatives of formula X



wherein  $\text{R}^{24}$  is an OH group, a  $\text{NH}_2$  group or a  $\text{NHR}^{25}$  group, in which  $\text{R}^{25}$  is a  $\text{C}_1$  to  $\text{C}_4$  alkyl group or a  $\text{C}_1$  to  $\text{C}_4$  hydroxyalkyl, or

(vi) 3,4-diaminobenzoic acid, or

(vii) combinations thereof; and

(B) oxidatively developing the coloring composition using atmospheric oxygen, an enzyme containing system, or combinations thereof as the sole oxidizing agent.

27. (NEW) The method of claim 26 wherein the pyrimidine derivative is 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-2,5,6-triaminopyrimidine, 2,4,5,6-tetraaminopyrimidine, 5,6-diamino-2,4-dihydroxypyrimidine, 2,4-diamino-5,6-dihydroxypyrimidine, or 4-methylamino-2,5,6-tetraminopyrimidine or combinations thereof.

28. (NEW) The method of claim 27 wherein the pyrimidine derivative is 2,4,5,6-tetraaminopyrimidine.

29. (NEW) The method of claim 26 wherein at least one of R<sup>7</sup> and R<sup>8</sup> of the Formula III is a C<sub>1</sub> to C<sub>4</sub> alkyl group or a C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl group, and wherein R<sup>20</sup> of the Formula VIII is hydrogen or a C<sub>1</sub> to C<sub>4</sub> alkoxy group.

30. (NEW) The method of claim 26 wherein the component B comprises 1,3-bis(2,4-diaminophenoxypropane), 1,3-bis(2,4-diaminophenylpropane), 2,4-diaminophenoxyethanol, 2,6-bis(2'-hydroxyethylamino)toluene, 3-amino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 2,4-dichloro-3-aminophenol, 3,5-diamino-2,6-dimethoxypyridine, 5-methylresorcinol, 2,5-dimethylresorcinol, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline, or N-(2-hydroxyethyl)-3,4-methylenedioxyaniline or combinations thereof.

**REMARKS**

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

**Status of Claims**

Claims 14 to 30 will be pending after entry of the present amendment. Claim 1 is being canceled without prejudice.

**Amendment**

The specification is being amended on page 23 to delete "lacuna" which is a typographical error.

New Claims 14 to 30 replace original Claims 1 to 13, and are being presented to better conform with US patent practice. These new claims are supported by the specification for example as shown in the Table below (cites to the specification are for the English translation):

Claim	Support in Specification
14, 26	page 3, line 24 to page 7, line 19, page 10, line 26 to page 10, line 10, page 21, line 15 to page 22, line 25, page 24, line 25 to page 25, line 3
15, 16, 27, 28	page 7, line 30 to page 8, line 7
17	page 8, lines 11 to 15
18, 29	page 4, line 17 to page 5, line 12, page 6, lines 1 to 22
19, 30	page 8, lines 18 to 28
20	page 8, lines 29 to 32
21	page 9, line 29 to page 10, line 11
22, 23	page 9, lines 3 to 18
24	page 12, lines 22 to 30
25	page 24, line 25 to page 25, line 3

No new matter is added by the new claims or amendments to the specification.

Docket No. H3294 PCT/US  
Application Serial No. 09/869,171  
PCT/EP99/09901

CONCLUSION

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,

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Agent for Coloring Keratinaceous Fibers

The invention relates to an agent for dyeing keratin fibers, in particular human hair, which comprises pyrimidine derivatives in combination with special couplers, to the use of this combination as  
5 dyeing component in hair dyeing agents, and to a method of dyeing keratin fibers, in particular human hair.

For the dyeing of keratin fibers, e.g. hair, wool or furs, use is generally made either of substantive dyes or oxidation dyes which are formed by oxidative  
10 coupling of one or more developer component with one another or with one or more coupler components. Coupler and developer components are also referred to as oxidation dye precursors.

The developer components usually used are primary  
15 aromatic amines having a further free or substituted hydroxyl or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazolone derivatives, and 2,4,5,6-tetraamino-pyrimidine and derivatives thereof.

Specific representatives are, for example,  
20 p-phenylene-diamine, p-toluylenediamine, 2,4,5,6-tetraaminopyrimidine, p-aminophenol, N,N-bis(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenyl)ethanol, 2-(2,5-diaminophenoxy)ethanol,  
25 1-phenyl-3-carboxyamido-4-aminopyrazol-5-one, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triamino-4-hydroxypyrimidine.

30 The coupler components usually used are m-phenylene-diamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones and m-aminophenols. Particularly suitable as coupler

substances are  $\alpha$ -naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 5-amino-2-methylphenol, m-aminophenol, resorcinol, resorcinol monomethyl ether, m-phenylenediamine, 2,4-diaminophenoxyethanol, 1-phenyl-3-methylpyrazol-5-one, 2,4-dichloro-3-aminophenol, 1,3-bis(2,4-diaminophenoxy)propane, 2-chlororesorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methylresorcinol and 5-methylresorcinol.

- 10 German patent application DE-A1-41 15 148 discloses oxidation dyeing agents which, in a cosmetic carrier, comprise a 2,4,5,6-tetraaminopyrimidine or a 6-hydroxy-2,4-triaminopyridine as oxidation base (developer) and a combination of certain green couplers and violet couplers for producing brilliant and washfast black colorations.

- With regard to further customary dye components, reference is made specifically to the "Dermatology" series, published by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, vol. 7, Ch. Zviak, The Science of Hair Care, chapter 7, pages 248-250 (substantive dyes), and chapter 8, pages 264-267 (oxidation dyes), and the "European Inventory of Cosmetic Raw Materials", 1996, published by the European Commission, available in diskette format from the Bundesverband der deutschen Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel e.V., Mannheim.

- Although intensive colorations with good fastness properties can be achieved with oxidation dyes, the development of the color, however, generally takes place under the influence of oxidizing agents, such as, for example,  $H_2O_2$ , which in some cases can result in damage to the fibers. Furthermore, some oxidation dye precursors or certain mixtures of oxidation dye precursors can occasionally have a sensitizing effect in people with sensitive skin. Although substantive dyes are applied under more moderate conditions, their

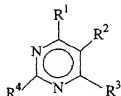
disadvantage is that the colorations frequently have inadequate fastness properties.

It is an object of the present invention to provide a dyeing agent for keratin fibers, in particular human hair, which is oxidizable by atmospheric oxygen, i.e. is not necessarily dependent on oxidizing agents, such as, for example,  $H_2O_2$ . The agent should be able to be applied to the fibers in a simple manner and, with regard to depth of color, gray coverage and fastness properties, are at least equal in qualitative terms to otherwise customary oxidation hair dyeing agents. Moreover, the dyeing agents must have no, or only a very low, sensitizing potential. It was a further object to find a dyeing system that allows blue shades to be produced on the keratin fiber by components specifically matched to one another.

Surprisingly, it has now been found that pyrimidine derivatives in combination with special couplers are highly suitable for the dyeing of keratin fibers, even in the absence of oxidizing agents i.e. in the presence of atmospheric oxygen. They produce colorations with excellent brilliance and depth of color and lead to a wide variety of color shades. However, the use of oxidizing agents should not in principle be excluded here.

The invention provides an agent for the dyeing of keratin fibers, in particular human hair, comprising

A) at least one pyrimidine derivative of the general formula I



(I)

in which  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  may be identical or different and are hydrogen, OH,  $NH_2$

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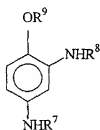


or a group  $\text{NR}^5\text{R}^6$ , in which  $\text{R}^5$  and  $\text{R}^6$  may be identical or different and are  $\text{C}_1\text{-C}_4\text{-alkyl}$ ,  $\text{C}_1\text{-C}_4\text{-hydroxyalkyl}$  having a primary and/or secondary hydroxyl group,

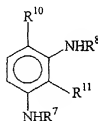
where two of the radicals  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  or  $\text{R}^4$  together can form an optionally substituted 5- and 6-membered heterocycle containing one or two nitrogen and/or oxygen atom(s) in the molecule,

with the proviso that at least two of the radicals  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  or  $\text{R}^4$  are a group  $\text{NH}_2$  and/or  $\text{NR}^5\text{R}^6$ ,

- B) at least one compound chosen from the group consisting of  
 (a) m-phenylene derivatives of the formulae II and III

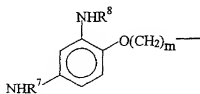


(II)



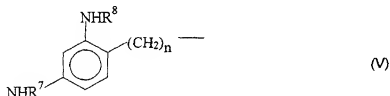
(III)

in which  $\text{R}^7$  and  $\text{R}^8$  may be identical or different and are hydrogen,  $\text{C}_1\text{-C}_4\text{-alkyl}$  or  $\text{C}_1\text{-C}_4\text{-hydroxyalkyl}$ ,  
 $\text{R}^9$  is  $\text{C}_1\text{-C}_4\text{-hydroxyalkyl}$  or a radical of the general formula IV



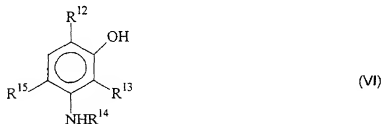
(IV)

in which  $R^7$  and  $R^8$  are as defined above and  $m$   
 is an integer from 1 to 4,  
 $R^{10}$  is hydrogen or a radical of the general  
 formula V



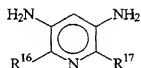
in which  $R^7$  and  $R^8$  are as defined above and  $n$   
 is an integer from 1 to 4,  
 $R^{11}$  is hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -  
 hydroxyalkyl,

(b)  $m$ -aminophenol derivatives



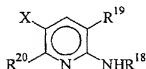
in which  $R^{12}$  is hydrogen or  $C_1$ - $C_4$ -alkyl,  
 $R^{13}$  is hydrogen, fluorine, chlorine,  
 $OCH_3$  or  $C_1$ - $C_4$ -alkyl,  
 $R^{14}$  is hydrogen,  $C_1$ - $C_4$ -alkyl,  $C_1$ - $C_4$ -  
 hydroxyalkyl or  $OCF_3$ ,  
 $R^{15}$  is hydrogen, fluorine, chlorine or  
 $OCH_3$ ,  
 with the provisos that  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$   
 and  $R^{15}$  are not hydrogen at the same  
 time and that, if  $R^{12}$  is methyl,  $R^{13}$ ,  
 $R^{14}$  and  $R^{15}$  are not hydrogen at the  
 same time,

- (c) pyridine derivatives of the formulae VII and VIII



(VII)

in which R<sup>16</sup> and R<sup>17</sup> may be identical or different and are fluorine, chlorine or OCH<sub>3</sub>,



(VIII)

in which R<sup>18</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkyl or C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl,

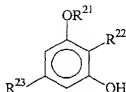
R<sup>19</sup> is OH or NH<sub>2</sub>,

R<sup>20</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkoxy or NH<sub>2</sub>,

X is hydrogen or OCH<sub>3</sub>,

with the provisos that, if R<sup>19</sup> is NH<sub>2</sub>, R<sup>18</sup> and R<sup>20</sup> are not C<sub>1</sub>-C<sub>4</sub>-alkyl or methoxy respectively at the same time, and if R<sup>18</sup> is hydrogen, R<sup>19</sup> and R<sup>20</sup> are not OH or hydrogen respectively at the same time,

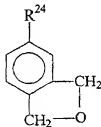
- (d) resorcinol derivatives of the formula IX



(IX)

in which  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  may be identical or different and are hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl, with the provisos that  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  are not hydrogen at the same time, if  $R^{21}$  and  $R^{23}$  are hydrogen,  $R^{22}$  is not methyl, and if  $R^{21}$  is methyl,  $R^{22}$  and  $R^{23}$  are not hydrogen at the same time,

(e) methylenedioxybenzene derivatives of the formula X



(X)

in which  $R^{24}$  is OH,  $NH_2$  or  $NHR^{25}$ , in which  $R^{25}$  is  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl, and

(f) 3,4-diaminobenzoic acid.

Keratin fibers are to be understood as meaning wool, furs, feathers and, in particular, human hair. In principle, however, the dyes according to the invention may also be used for the dyeing of other natural fibers, such as, for example, cotton, jute, sisal, linen or silk, modified natural fibers, such as, for example, regenerated cellulose, nitro-, alkyl- or hydroxyalkyl- or acetylcellulose, and synthetic fibers, such as, for example, polyamide, polyacrylonitrile, polyurethane and polyester fibers.

The pyrimidine derivatives of the formula I used according to the invention are preferably chosen from the group consisting of 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-2,5,6-triaminopyrimidine,

2,4,5,6-tetraaminopyrimidine, 5,6-diamino-2,4-dihydroxypyrimidine, 2,4-diamino-5,6-dihydroxypyrimidine, 4-dimethylamino-2,5,6-tetraaminopyrimidine. Particular preference is given to using 2,4,5,6-tetraaminopyrimidine, 4-dimethylamino-2,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine and 5,6-diamino-2,4-dihydroxypyrimidine.

These substances are known from the literature or are available commercially.

The aforementioned pyrimidine derivatives of the formula I are preferably used in the agents according to the invention in an amount of from 0.03 to 65 mmol, in particular from 1 to 40 mmol, based on 100 g of the total dyeing agent.

Of the compounds of the formula VIII, preference is given to those in which X is hydrogen.

Couplers of component B are preferably chosen from the group 1,3-bis(2,4-diaminophenoxypropane), 1,3-bis(2,4-diaminophenylpropane), 2,4-diaminophenoxyethanol, 2,6-bis(2'-hydroxyethylamino)toluene, 3-amino-2-chloro-6-methylphenyl, 5-amino-4-chloro-2-methylphenol, 2,4-dichloro-3-aminophenol, 3,5-diamino-2,6-dimethoxypyridine, 5-methylresorcinol, 2,5-dimethylresorcinol, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline, N-(2-hydroxyethyl)-3,4-methylenedioxyaniline and any mixtures of the above.

The aforementioned compounds of component B can be used in an amount of, in each case, 0.03 to 65 mmol, in particular 1 to 40 mmol, in each case based on 100 g of the total dyeing agent.

In all of the dyeing agents it is also possible to use two or more different pyrimidine derivatives of the formula I together; likewise, it is also possible to use two or more different compounds of component B together. This embodiment also covers the use of substances which represent reaction products of

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pyrimidine derivatives of the formula I with said compounds of component B.

The color shades can also be further varied and intensified if one or more compounds chosen from 5,6-dihydroxyindole and its N-substituted C<sub>1</sub>-C<sub>4</sub>-alkyl and C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl derivatives, 5,6-dihydroxyindoline and its N-substituted C<sub>1</sub>-C<sub>4</sub>-alkyl and C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl derivatives and the compounds known as developers, chosen from the group consisting of p-phenylenediamine, p-tolylenediamine, p-aminophenol, 4,4'-diaminodiphenylamine, 1,10-bis(2,5-diaminophenyl)-1,4,7,10-tetraoxydecane, 2, (2'-hydroxyethyl)-p-phenylenediamine, 2,6-dichloro-4-aminophenol, N,N-bis(2'-hydroxyethyl)-p-phenylenediamine, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 5-aminosalicylic acid, bis(2-hydroxy-5-aminophenyl)methane and 2-(2,5-diaminophenoxy)ethanol are added to the agent according to the invention.

A further preferred developer component is 4-amino-2-((diethylamino)methyl)phenol.

Particularly preferred developer components are, for example, p-phenylenediamine, p-tolylenediamine, 1,10-bis(2,5-diaminophenyl)-1,4,7,10-tetraoxydecane, 2, (2'-hydroxyethyl)-p-phenylenediamine, 2,6-dichloro-4-aminophenol, N,N-bis(2'-hydroxyethyl)-p-phenylenediamine, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 4-amino-2-((diethylamino)methyl)phenol and bis(2-hydroxy-5-aminophenyl)methane.

In a further preferred embodiment, activated carbonyl compounds and further substances known as developers or couplers are added to the combination according to the invention of components A and B to further modify the color shades.

Examples of activated carbonyl compounds are isatin, 5-chloroisatin, 5-bromoisatin, 6-bromoisatin, 5-nitroisatin, N-hydroxymethylisatin, N-allylisatin, 5-isatinsulfonic acid Na salt, glutaconaldehyde tetrabutylammonium salt, tribase aldehyde,

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malonaldehyde bis(dimethyl acetal), 4-hydroxy-3-methoxycinnanaldehyde, 1-piperidinomethylisatin, 1-diethylaminomethylisatin, glutacetaldehyde Na salt, 5-N-methylanilinopentadienyl, 2-chloro-3-hydroxy-methylene-1-cyclohexene 1-aldehyde, N-(5-anilino-2,4-pentanedien-1-ylidene)anilinium chloride, trans- $\beta$ -(2-furyl)acrolein, 2-nitro-1,3-indanedione, dehydroascorbic acid, 2-acetyl-1,3-cyclohexanedione, 7-dimethylamino-2,4,6-heptatrienylidene dimethylammonium perchlorate and 4-formyl-1-methylpyridinium benzenesulfonate.

Examples of couplers which may additionally be present are 3-amino-2-methylamino-6-methoxypyridine, 2-amino-4-(2'-hydroxyethylamino)anisole,  $\alpha$ -naphthol, resorcinol, resorcinol monomethyl ether, 4-chlororesorcinol, 2-methylresorcinol, m-aminophenol, 3-N,N-dimethylaminophenol, 5-amino-2-methoxyphenol, 5-amino-2-methylphenol, 3-amino-2,4-dimethylphenol, 3-(N-cyclopentyl)aminophenol, 1,5-, 1,7-, 2,7-dihydroxynaphthalenes, o-aminophenol, 6-hydroxybenzomorpholine, 1-phenyl-3-methylpyrazol-5-one, 2-amino-6-methylphenol, 2,6-dihydroxy-3,4-dimethylpyridine, 4-hydroxyindole, 6-hydroxyindole, 7-hydroxyindole, 4-aminoindole and 2,4-diamino-5-methylphenetole.

The dyeing agent according to the invention represents an air-oxidizable system. In this connection, it is possible to dispense with additional oxidizing agents, e.g.  $H_2O_2$ . In some circumstances, however, it may be desirable to add hydrogen peroxide or other oxidizing agents, such as peroxydisulfate or percarbonate, to the agents according to the invention to achieve shades which are paler than keratin fibers to be dyed. Furthermore, in some circumstances, it is possible, in the absence of oxidizing agents, i.e. whether atmospheric oxygen or hydrogen peroxide is used, to establish different color shades. Oxidizing agents are generally used in an amount of from 0.01 to

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6% by weight, based on the use solution. An oxidizing agent preferred for human hair is H<sub>2</sub>O<sub>2</sub>.

Furthermore, it is possible to carry out the oxidation using enzymes. Here, the enzymes can be used  
5 either to generate oxidizing percompounds, and to intensify the effect of a small amount of oxidizing agent present. Examples of enzymatic processes are the use of laccases and the intensification of the effect of small amounts (e.g. 1% and less, based on the total  
10 agent) of hydrogen peroxide by peroxidases.

In a preferred embodiment, the dyes according to the invention comprise, for the further modification of the color shades, in addition to the compounds present according to the invention, additionally customary  
15 substantive dyes, e.g. from the group of nitrophenylenediamines, nitroaminophenols, anthraquinones or indophenols, such as, for example, the compounds known under the international designations or trade names HC Yellow 2, HC Yellow 4, HC Yellow 6,  
20 Basic Yellow 57, Disperse Orange 3, HC Red 3, HC Red BN, Basic Red 76, HC Blue 2, Disperse Blue 3, Basic Blue 99, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Basic Brown 16 and Basic Brown 17, and also picramic acid, 2-amino-6-chloro-  
25 4-nitrophenol, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, 4-N-ethyl-1,4-bis(2'-hydroxyethylamino)-2-nitrobenzene hydrochloride and 1-methyl-3-nitro-4-(2'-hydroxyethyl)aminobenzene. The inventive agents according to  
30 this embodiment preferably comprise the substantive dyes in an amount of from 0.01 to 20% by weight, based on the total dyeing agent.

Furthermore, the preparations according to the invention can also comprise naturally occurring dyes  
35 such as, for example, henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea, buckthorn bark, sage, logwood, madder root, catechu, sedre and alkanna root.

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It is not necessary for the oxidation dye precursors or the optionally present substantive dyes to each represent uniform compounds. Rather, it is possible that, as a result of the preparation processes  
5 for the individual dyes, further components are present in minor amounts in the dyeing agents according to the invention, provided these do not adversely impair the dyeing result, or have to be excluded for other reasons, e.g. toxicological reasons.

10 The dyeing agents according to the invention produce intensive colorations even at physiologically compatible temperatures of less than 45°C. They are therefore particularly suitable for the dyeing of human hair. For use on human hair, the dyeing agents can  
15 usually be incorporated into a hydrous cosmetic carrier. Suitable hydrous cosmetic carriers are e.g. creams, emulsions, gels and also surfactant-containing foaming solutions such as e.g. shampoos or other preparations which are suitable for use on the keratin  
20 fibers. If necessary, it is also possible to incorporate the dyeing agents into anhydrous carriers.

Furthermore, the dyeing agents according to the invention can comprise all active ingredients, additives and auxiliaries known in such preparations.  
25 In many cases, the dyeing agents comprise at least one surfactant, where, in principle, both anionic and also zwitterionic, ampholytic, nonionic and cationic surfactants are suitable. However, in many cases it has proven advantageous to choose the surfactants from  
30 anionic, zwitterionic or nonionic surfactants.

Suitable anionic surfactants in preparations according to the invention are all anionic surface-active substances suitable for use on the human body. These are characterized by a solubilizing anionic  
35 group, such as, for example, a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group having about 10 to 22 carbon atoms. Additionally, glycol or polyglycol ether groups, ester, ether and

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amide groups and hydroxyl groups may be present in the molecule. Examples of suitable anionic surfactants are, in each case in the form of the sodium, potassium or ammonium and the mono-, di- and trialkanolammonium salts having 2 or 3 carbon atoms in the alkanol group,

- linear fatty acids having 10 to 22 carbon atoms (soaps)
- ether carboxylic acids of the formula  $R-O-(CH_2-CH_2O)_x-CH_2-COOH$ , in which R is a linear alkyl group having 10 to 22 carbon atoms and  $x = 0$  or 1 to 16,
- acyl sarcosides having 10 to 18 carbon atoms in the acyl group,
- acyl taurides having 10 to 18 carbon atoms in the acyl group,
- acyl isethionates having 10 to 18 carbon atoms in the acyl group,
- sulfosuccinic mono- and dialkyl esters having 8 to 18 carbon atoms in the alkyl group and sulfosuccinic monoalkylpolyoxyethyl esters having 8 to 18 carbon atoms in the alkyl group and 1 to 6 oxyethyl groups,
- linear alkanesulfonates having 12 to 18 carbon atoms,
- linear alpha-olefinsulfonates having 12 to 18 carbon atoms,
- alpha-sulfo fatty acid methyl esters of fatty acids having 12 to 18 carbon atoms,
- alkyl sulfates and alkylpolyglycol ether sulfates of the formula  $R-O(CH_2-CH_2O)_x-SO_3H$ , in which R is a preferably linear alkyl group having 10 to 18 carbon atoms and  $x = 0$  or 1 to 12,
- mixtures of surface-active hydroxysulfonates according to DE-A-37 25 030,
- sulfated hydroxyalkyl polyethylene and/or hydroxyalkylene propylene glycol ethers according to DE-A-37 23 354,

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- sulfonates of unsaturated fatty acids having 12 to 24 carbon atoms and 1 to 6 double bonds according to DE-A-39 26 344,
  - esters of tartaric acid and citric acid with
- 5 alcohols, which represent addition products of approximately 2 to 15 molecules of ethylene oxide and/or propylene oxide to fatty alcohols having 8 to 22 carbon atoms.

10 Preferred anionic surfactants are alkyl sulfates, alkylpolyglycol ether sulfates and ether carboxylic acids having 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule, and in particular salts of saturated and in particular

15 unsaturated C<sub>8</sub>-C<sub>22</sub>-carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

Zwitterionic surfactants is the term used for those surface-active compounds which carry at least one quaternary ammonium group and at least one -COO<sup>(-)</sup> or -SO<sub>3</sub><sup>(-)</sup> group in the molecule. Particularly suitable

20 zwitterionic surfactants are the betaines, such as the N-alkyl-N,N-dimethylammonium glycinate, for example the cocoalkyldimethylammonium glycinate, N-acylaminopropyl-N,N-dimethylammonium glycinate, for

25 example the cocoacylaminopropyldimethylammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethylimidazolines having in each case 8 to 18 carbon atoms in the alkyl or acyl group, and cocoacylaminoethyl hydroxyethylcarboxymethylglycinate.

30 A preferred zwitterionic surfactant is the fatty acid amide derivative known under the CTFA name Cocamidopropyl Betaine.

Ampholytic surfactants are understood as meaning those surface-active compounds which, apart from a

35 C<sub>8</sub>-18-alkyl or -acyl group in the molecule, contain at least one free amino group and at least one -COOH or -SO<sub>3</sub>H group and are capable of forming internal salts. Examples of suitable ampholytic surfactants are

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N-alkylglycines, N-alkylpropionic acids, N-alkylaminobutyric acids, N-alkylaminodipropionic acids, N-hydroxyethyl-N-alkylamidopropylglycines, N-alkyltaurines, N-alkylsarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids having in each case about 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkylaminopropionate, cocoacylaminoethylaminopropionate and C<sub>12-18</sub>-acylsarcosine.

Nonionic surfactants comprise, as hydrophilic group, e.g. a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether group. Such compounds are, for example,

- addition products of 2 to 30 mol of ethylene oxide and/or 0 to 5 mol of propylene oxide to linear fatty alcohols having 8 to 22 carbon atoms, to fatty acids having 12 to 22 carbon atoms and to alkyl phenols having 8 to 15 carbon atoms in the alkyl group,
- C<sub>12-22</sub>-fatty acid mono- and diesters of addition products of from 1 to 30 mol of ethylene oxide to glycerol,
- C<sub>8-22</sub>-alkyl mono- and oligoglycosides and ethoxylated analogs thereof,
- addition products of from 5 to 60 mol of ethylene oxide to castor oil and hydrogenated castor oil,
- addition products of ethylene oxide to sorbitan fatty acid esters
- addition products of ethylene oxide to fatty acid alkanolamides.

Examples of the cationic surfactants to be used in the hair-treatment agents according to the invention are, in particular, quaternary ammonium compounds. Preference is given to ammonium halides, such as alkyltrimethylammonium chlorides, dialkyldimethyl-

ammonium chlorides and trialkylmethylammonium chlorides, e.g. cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, distearyldimethylammonium chloride, lauryldimethylammonium chloride, 5 lauryldimethylbenzylammonium chloride and tricetylmethylammonium chloride. Further cationic surfactants which can be used according to the invention are the quaternized protein hydrolysates.

Likewise suitable for the invention are cationic 10 silicone oils, such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethylsilylamodimethicone), Dow Corning 949 emulsion (comprising a hydroxylamino-modified silicone, which is also referred to as amodimethicone), 15 SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, Quaternium-80).

Alkylamidoamines, in particular fatty acid 20 amidoamines, such as stearylamidopropyldimethylamine obtainable under the name Tego Amid®S 18, are distinguished not only by a good conditioning action, but specifically by their good biodegradability.

Likewise very biodegradable are quaternary ester 25 compounds, "ester quats", such as the methylhydroxyalkyldialkoyloxyalkylammonium methosulfates sold under the trade name Stepantex®.

An example of a quaternary sugar derivative which can be used as cationic surfactant is the commercial 30 product Glucquat® 100, according to CTFA nomenclature a "Lauryl Methyl Gluceth-10 Hydroxypropyl Dimonium Chloride".

The compounds containing alkyl groups which are used as surfactants may each be uniform substances. 35 However, it is generally preferred to start from natural vegetable or animal raw materials for the preparation of these substances, thus giving substance

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mixtures having varying alkyl chain lengths depending on the respective raw material.

In the case of the surfactants which represent additional products of ethylene and/or propylene oxide to fatty alcohols or derivatives of these addition products, it is possible to use either products with a "normal" homolog distribution, or those with a narrowed homolog distribution. "Normal" homolog distribution is understood as meaning here mixtures of homologs obtained during the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alkoxides as catalysts. Narrowed homolog distributions are, by contrast, obtained if, for example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alkoxides are used as catalysts. The use of products having narrowed homolog distribution may be preferable.

Further active ingredients, auxiliaries and additives are, for example,

- nonionic polymers such as, for example, vinylpyrrolidone/vinyl acrylate copolymers, polyvinylpyrrolidone and vinylpyrrolidone/vinyl acetate copolymers and polysiloxanes,
- 25 - cationic polymers, such as quaternized cellulose ethers, polysiloxanes containing quaternary groups, dimethyldiallylammonium chloride polymers, acrylamide-dimethyldiallylammonium chloride copolymers, dimethylaminoethyl methacrylate-vinylpyrrolidone copolymers quaternized with
- 30 diethyl sulfate, vinylpyrrolidone-imidazolinium methochloride copolymers and quaternized polyvinyl alcohol,
- zwitterionic and amphoteric polymers such as, for
- 35 example, acrylamidopropyltrimethylammonium chloride/acrylate copolymers and octylacrylamide/methyl methacrylate/tert-butylaminoethyl

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- methacrylate/2-hydroxypropyl methacrylate  
copolymers,
- 5 - anionic polymers such as, for example, polyacrylic  
acids, crosslinked polyacrylic acids, vinyl  
acetate/crotonic acid copolymers, vinyl  
pyrrolidone/vinyl acrylate copolymers, vinyl  
acetate/butyl maleate/isobornyl acrylate  
copolymers, methyl vinyl ether/maleic anhydride  
copolymers and acrylic acid/ethyl acrylate/N-tert-  
10 butylacrylamide terpolymers,
- thickeners, such as agar agar, guar gum,  
alginates, xanthan gum, gum arabic, karaya gum,  
carob bean flour, linseed gums, dextrans,  
cellulose derivatives, e.g. methylcellulose,  
15 hydroxyalkylcellulose and carboxymethylcellulose,  
starch fractions and derivatives such as amylose,  
amylopectin and dextrans, clays such as, for  
example, bentonite or fully synthetic  
hydrocolloids such as, for example, polyvinyl  
20 alcohol,
- structurants, such glucose and maleic acid,  
- hair-conditioning compounds, such as  
phospholipids, for example soya lecithin, egg  
lecithin and cephalins, and silicone oils,  
25 - protein hydrolysates, in particular elastin,  
collagen, keratin, milk protein, soya protein and  
wheat protein hydrolysates, condensation products  
thereof with fatty acids, and quaternized protein  
hydrolysates,
- 30 - perfume oils, dimethyl isosorbide and  
cyclodextrins,
- solubility promoters, such as ethanol,  
isopropanol, ethylene glycol, propylene glycol,  
glycerol and diethylene glycol,
- 35 - antidandruff agents, such as Piroctone Olamine and  
Zinc Omadine,
- further substances for adjusting the pH,

- active ingredients, such as panthenol, pantothenic acid, allantoin, pyrrolidonecarboxylic acids and salts thereof, plant extracts and vitamins,
- cholesterol,
- 5 - light protection agents,
- consistency regulators, such as sugar esters, polyol esters or polyol alkyl ethers,
- fats and waxes, such as spermaceti, beeswax, montan wax, paraffins, fatty alcohols and fatty acid esters,
- 10 - fatty acid alkanolamides,
- complexing agents, such as EDTA, NTA and phosphonic acids,
- swelling and penetration substances, such as
- 15 glycerol, propylene glycol monoethyl ether, carbonates, hydrogencarbonates, guanidines, ureas, and primary, secondary and tertiary phosphates, imidazoles, tannins, pyrrole,
- opacifiers, such as latex,
- 20 - pearlizing agents, such as ethylene glycol mono- and distearate,
- propellants, such as propane/butane mixtures, N<sub>2</sub>O, dimethyl ether, CO<sub>2</sub> and air, and
- antioxidants.

25 The constituents of the hydrous carrier are used for the preparation of the dyeing agents according to the invention in amounts customary for this purpose; e.g. emulsifiers are used in concentrations of from 0.5 to 30% by weight, and thickeners are used in

30 concentrations of from 0.1 to 25% by weight, of the total dyeing agent.

For the dyeing result, it may be advantageous to add ammonium or metal salts to the dyeing agents. Suitable metal salts are e.g. formates, carbonates,

35 halides, sulfates, butyrates, valerates, caproates, acetates, lactates, glycolates, tartrates, citrates, gluconates, propionates, phosphates and phosphonates of alkali metals, such as potassium, sodium or lithium,

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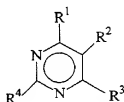


alkaline earth metals, such as magnesium, calcium, strontium or barium, or of aluminum, manganese, iron, cobalt, copper or zinc, preference being given to sodium acetate, lithium bromide, calcium bromide, calcium gluconate, zinc chloride, zinc sulfate, magnesium chloride, magnesium sulfate, ammonium carbonate, chloride and acetate. These salts are preferably present in an amount of from 0.03 to 65 mmol, in particular from 1 to 40 mmol, based on 100 g of the total dyeing agent.

The pH of the ready-to-use dyeing preparations is usually between 2 and 11, preferably between 5 and 9.

The present invention further provides for the use of a combination of

- A) at least one pyrimidine derivative of the general formula I



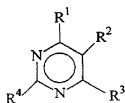
(I)

- in which R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may be identical or different and are hydrogen, OH, NH<sub>2</sub> or a group NR<sup>5</sup>R<sup>6</sup>, in which R<sup>5</sup> and R<sup>6</sup> may be identical or different and are C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl having a primary and/or secondary hydroxyl group, where two of the radicals R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> together can form an optionally substituted 5- and 6-membered heterocycle containing one or two nitrogen and/or oxygen atom(s) in the molecule, with the proviso that at least two of the radicals R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> are a group NH<sub>2</sub> and/or NR<sup>5</sup>R<sup>6</sup>,

- B) at least one compound chosen from the group consisting of the (a) m-phenylenediamine derivatives of the general formulae II or III, (b) m-aminophenol derivatives of the general formula VI, (c) pyridine derivatives of the formulae VII or VIII, (d) resorcinol derivatives of the formula IX, (e) methyldioxybenzene derivatives of the formula X or (f) 3,4-diaminobenzoic acid, which are shown above,
- 10 for dyeing keratin fibers.

The present invention also further provides a method of dyeing keratin fibers, in particular human hair, in which a dyeing agent comprising

- 15 A) at least one pyrimidine derivative of the general formula I,



(I)

- 20 in which R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> may be identical or different and are hydrogen, OH, NH<sub>2</sub> or a group NR<sup>5</sup>R<sup>6</sup>, in which R<sup>5</sup> and R<sup>6</sup> may be identical or different and are C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl having a
- 25 primary and/or secondary hydroxyl group, where two of the radicals R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> together can form an optionally substituted 5- and 6-membered heterocycle containing one or two
- 30 nitrogen and/or oxygen atom(s) in the molecule,
- with the proviso that at least two of the radicals R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> or R<sup>4</sup> are a group NH<sub>2</sub> and/or NR<sup>5</sup>R<sup>6</sup>,

5 B) at least one compound chosen from the group consisting of the (a) m-phenylenediamine derivatives of the general formulae II or III, (b) m-aminophenol derivatives of the general formula VI, (c) pyridine derivatives of the formulae VII or VIII, (d) resorcinol derivatives of the formula IX, (e) methyldioxybenzene derivatives of the formula X or (f) 3,4-diaminobenzoic acid, and customary cosmetic ingredients, is applied to the  
10 keratin fibers, left on the fibers for a while, usually about 30 minutes, and then rinsed out again or washed out using a shampoo.

15 The pyrimidine derivatives of the formula I and the compounds of component B can either be applied to the hair simultaneously or one after the other, it being unimportant which of the two components is applied first. If it is necessary to achieve a certain color shade, any oxidizing agent used is also applied in this stage together with the other components, or  
20 subsequently. The optionally present ammonium or metal salts may be added to the first or the second component. There may be an interval of up to 30 minutes between application of the first component and that of the second component. Pretreatment of the fibers with  
25 the salt solution is also possible.

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Examples

Hair dyeing agents according to the invention were  
 [lacuna] in the form of a hair dyeing cream emulsion of  
 5 the composition given in Table 1.

Table 1

Component	1	2	3	4	5	6	7
	% by wt.						
C <sub>12</sub> -C <sub>14</sub> -fatty alcohol + 2 EO sulfate, Na salt, 28% strength solution	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Cocoamidopropylbetaine, 30% strength	12.5	12.5	12.5	12.5	12.5	12.5	12.5
C <sub>10</sub> -C <sub>18</sub> fatty alcohol	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Tallow fatty alcohol	8.5	8.5	8.5	8.5	8.5	8.5	8.5
C <sub>16</sub> -C <sub>18</sub> fatty alcohol + 20 EO	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Ammonium sulfate	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sodium sulfate	0.1	0.1	0.1	0.1	0.1	0.1	0.1
4-Hydroxy-2,5,6-tri- aminopyrimidine sulfate	2.4	2.4	2.4	2.4	2.4	2.4	2.4
2,4-Diaminophenoxy- ethanol dihydrochloride	2.4	-	-	-	-	-	-
3,5-Diamino-2,6-di- methoxypyridine dihydrochloride	-	2.4	-	-	-	-	-
1,3-bis(2,4-Diamino- phenoxy)propane tetra- hydrochloride	-	-	4.7	2.12	1.18	-	-
N-Allylisatin	-	-	-	0.19	0.94	-	-
1,10-bis(2,5-Diamino- phenyl)-1,4,7-10-tetra- oxydecane tetrahydro- chloride	-	-	-	1.02	5.1	-	-
3-Amino-2-chloro-6- methylphenol	-	-	-	-	-	1.58	-
3,4-Methylenedioxyphenol	-	-	-	-	-	-	1.38
Water	ad 100						

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The individual constituents were mixed together at 70°C and, after cooling, adjusted to a pH of 9.5 with NaOH.

Using the compositions given in Table 1, colorations were carried out using H<sub>2</sub>O<sub>2</sub> as oxidizing agent and without oxidizing agent, i.e. by air oxidation.

For the oxidative development of the coloration using H<sub>2</sub>O<sub>2</sub>, the compositions shown in Table 1 were mixed with 12% strength hydrogen peroxide in the ratio 1:1. In the case of air oxidation, the compositions shown in Table 1 were mixed with water prior to use in the ratio 1:1.

The application mixture was applied to approximately 15 cm-long tresses of standardized, 90% gray human hair which has not been pretreated in any particular way, and left there for 30 minutes at 27°C. When the dyeing process was complete, the hair was rinsed, washed with a customary shampoo and then dried. The coloring results are shown in Table 2.

**Table 2**

Formulation No.	Color shade	
	H <sub>2</sub> O <sub>2</sub> oxidation	Air oxidation
1	Deep blue-violet	Deep blue-violet
2	Reddish mid-brown	Reddish mid-brown
3	Mid-dark brown	Mid-dark brown
4	-	Dark brown
5	-	Black
6	Gray magenta	Rich Bordeaux
7	Pale orange	Sand-colored

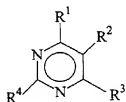
The dyeing results show that the agents according to the invention produce excellent coloring results both with and without the addition of oxidizing agents. Similar colorations are obtained if, in example 7, the

enzyme system glucose-oxidase/glucose/peroxidase or the enzyme system uricase/uric acid/peroxidase is used as oxidizing agent at pH = 8.5.

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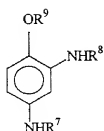
Patent claims

1. An agent for dyeing keratin fibers, comprising  
A) at least one pyrimidine derivative of the  
5 general formula I

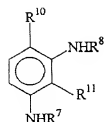


10 in which  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  may be identical or  
different and are hydrogen, OH,  $NH_2$   
or a group  $NR^5R^6$ , in which  $R^5$  and  $R^6$   
may be identical or different and are  
15  $C_1$ - $C_4$ -alkyl,  $C_1$ - $C_4$ -hydroxyalkyl having  
a primary and/or secondary hydroxyl  
group,  
where two of the radicals  $R^1$ ,  $R^2$ ,  $R^3$   
or  $R^4$  together can form an optionally  
substituted 5- and 6-membered  
20 heterocycle containing one or two  
nitrogen and/or oxygen atom(s) in the  
molecule,  
with the proviso that at least two of  
the radicals  $R^1$ ,  $R^2$ ,  $R^3$  or  $R^4$  are a  
group  $NH_2$  and/or  $NR^5R^6$ ,

- 25 B) at least one compound chosen from the group  
consisting of  
(a) m-phenylene derivatives of the  
formulae II and III

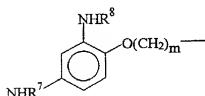


(II)



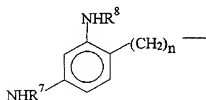
(III)

in which  $R^7$  and  $R^8$  may be identical or different and are hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl,  $R^9$  is  $C_1$ - $C_4$ -hydroxyalkyl or a radical of the general formula IV



(IV)

in which  $R^7$  and  $R^8$  are as defined above and  $m$  is an integer from 1 to 4,  $R^{10}$  is hydrogen or a radical of the general formula V

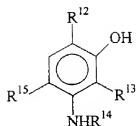


(V)

in which  $R^7$  and  $R^8$  are as defined above and  $n$  is an integer from 1 to 4,  $R^{11}$  is hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl,

(b) m-aminophenol derivatives

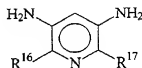




(VI)

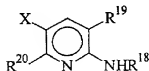
in which  $R^{12}$  is hydrogen or  $C_1$ - $C_4$ -alkyl,  
 $R^{13}$  is hydrogen, fluorine, chlorine,  
 $OCH_3$  or  $C_1$ - $C_4$ -alkyl,  
 $R^{14}$  is hydrogen,  $C_1$ - $C_4$ -alkyl,  $C_1$ - $C_4$ -  
hydroxyalkyl or  $OCF_3$ ,  
 $R^{15}$  is hydrogen, fluorine, chlorine or  
 $OCH_3$ ,  
with the provisos that  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  are  
not hydrogen at the same time and that, if  $R^{12}$   
is methyl,  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  are not hydrogen at  
the same time,

(c) pyridine derivatives of the formulae VII  
and VIII



(VII)

in which  $R^{16}$  and  $R^{17}$  may be identical or  
different and are fluorine, chlorine  
or  $-OCH_3$ ,



(VIII)

in which  $R^{18}$  is hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -  
hydroxyalkyl,

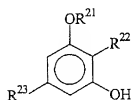
$R^{19}$  is OH or  $NH_2$ ,

$R^{20}$  is hydrogen,  $C_1$ - $C_4$ -alkoxy or  $NH_2$ ,

X is hydrogen or  $OCH_3$ ,

with the provisos that, if  $R^{19}$  is  $NH_2$ ,  $R^{18}$  and  $R^{20}$  are not  $C_1$ - $C_4$ -alkyl or methoxy respectively at the same time, and if  $R^{18}$  is hydrogen,  $R^{19}$  and  $R^{20}$  are not OH or hydrogen respectively at the same time,

(d) resorcinol derivatives of the formula IX

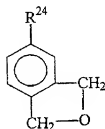


(IX)

in which  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  may be identical or different and are hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl,

with the provisos that  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  are not hydrogen at the same time, if  $R^{21}$  and  $R^{23}$  are hydrogen,  $R^{22}$  is not methyl, and if  $R^{21}$  is methyl,  $R^{22}$  and  $R^{23}$  are not hydrogen at the same time,

(e) methylenedioxybenzene derivatives of the formula X



(X)

in which  $R^{24}$  is OH,  $NH_2$  or  $NHR^{25}$ , in which  $R^{25}$  is  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl, and

(f) 3,4-diaminobenzoic acid.

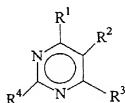
2. The agent as claimed in claim 1, characterized in that 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-2,5,6-triaminopyrimidine, 2,4,5,6-tetraaminopyrimidine, 5,6-diamino-2,4-dihydroxypyrimidine, 2,4-diamino-5,6-dihydroxypyrimidine, 4-dimethylamino-2,5,6-tetraminopyrimidine and any mixtures thereof are present as pyrimidine derivatives of the formula I.
3. The agent as claimed in claim 1 or 2, characterized in that the pyrimidine derivatives of the formula I are present in an amount of from 0.03 to 65 mmol, in particular from 1 to 40 mmol, based on 100 g of the total dyeing agent.
4. The agent as claimed in any of claims 1 to 3, characterized in that the compounds of component B are chosen from the group 1,3-bis(2,4-diaminophenoxypropane), 1,3-bis(2,4-diaminophenylpropane), 2,4-diaminophenoxyethanol, 2,6-bis(2'-hydroxyethylamino)toluene, 3-amino-2-chloro-6-methylphenyl, 5-amino-4-chloro-2-methylphenol, 2,4-dichloro-3-aminophenol, 3,5-diamino-2,6-dimethoxypyridine, 5-methylresorcinol, 2,5-dimethylresorcinol, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline, N-(2-hydroxyethyl)-3,4-methylenedioxyaniline and any mixtures thereof.
5. The agent as claimed in any of claims 1 to 4, characterized in that the compounds of component B are present in an amount of, in each case, from 0.03 to 65 mmol, in particular from 1 to 40 mmol, in each case based on 100 g of the total dyeing agent.
6. The agent as claimed in any of claims 1 to 5, characterized in that at least one activated

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carbonyl compound chosen from the group consisting of isatin, 5-chloroisatin, 5-bromoisatin, 6-bromoisatin, 5-nitroisatin, N-hydroxymethylisatin, N-allylisatin, 5-isatinsulfonic acid Na salt, glutacanaldehyde tetrabutylammonium salt, tribase aldehyde, malonaldehyde bis(dimethyl acetal), 4-hydroxy-3-methoxycinnanaldehyde, 1-piperidino-methylisatin, 1-diethylaminomethylisatin, glutacanaldehyde Na salt, 5-N-methylanilinopentadienyl, 2-chloro-3-hydroxymethylene-1-cyclohexene 1-aldehyde, N-(5-anilino-2,4-pentadien-1-ylidene)anilinium chloride, trans- $\beta$ -(2-furyl)-acrolein, 2-nitro-1,3-indanedione, dehydroascorbic acid, 2-acetyl-1,3-cyclohexanedione, 7-dimethylamino-2,4,6-heptatrienylidene dimethylammonium perchlorate and 4-formyl-1-methylpyridinium benzenesulfonate.

7. The agent as claimed in any of claims 1 to 6, characterized in that one or more compounds chosen from 5,6-dihydroxyindole and its N-substituted C<sub>1</sub>-C<sub>4</sub>-alkyl and C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl derivatives, 5,6-dihydroxyindoline and its N-substituted C<sub>1</sub>-C<sub>4</sub>-alkyl and C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl derivatives and the compounds known as developers, chosen from the group consisting of p-phenylenediamine, p-tolylenediamine, p-aminophenol, 4,4'-diaminodiphenylamine, 1,10-bis(2,5-diaminophenyl)-1,4,7,10-tetraoxydecane, 2-(2'-hydroxyethyl)-p-phenylenediamine, 2,6-dichloro-4-aminophenol, N,N-bis(2'-hydroxyethyl)-p-phenylenediamine, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 5-aminosalicylic acid, bis(2-hydroxy-5-aminophenyl)methane, 2-(2,5-diaminophenoxy)ethanol are also added.

8. The agent as claimed in any of claims 1 to 7, characterized in that it comprises anionic, zwitterionic or nonionic surfactants.
- 5 9. The agent as claimed in any of claims 1 to 8, characterized in that it is an air-oxidizable dyeing system.
- 10 10. The agent as claimed in any of claims 1 to 8, characterized in that [lacuna] comprises oxidizing agents chosen from the group  $H_2O_2$ , peroxydisulfate and percarbonate.
- 15 11. The agent as claimed in any of claims 1 to 8, characterized in that it is an enzymatic dyeing system.
- 20 12. The use of a combination of  
A) at least one pyrimidine derivative of the general formula I



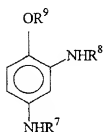
- 25 in which  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  may be identical or different and are hydrogen, OH,  $NH_2$  or a group  $NR^5R^6$ , in which  $R^5$  and  $R^6$  may be identical or different and are  $C_1$ - $C_4$ -alkyl,  $C_1$ - $C_4$ -hydroxyalkyl having a primary and/or secondary hydroxyl group,
- 30 where two of the radicals  $R^1$ ,  $R^2$ ,  $R^3$  or  $R^4$  together can form an optionally substituted 5- and 6-membered heterocycle containing one or two

nitrogen and/or oxygen atom(s) in the molecule,

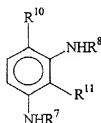
with the proviso that at least two of the radicals  $R^1$ ,  $R^2$ ,  $R^3$  or  $R^4$  are a group  $NH_2$  and/or  $NR^5R^6$ ,

B) at least one compound chosen from the group consisting of

(a) m-phenylene derivatives of the formulae II and III



(II)

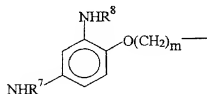


(III)

(II)

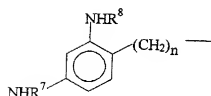
(III)

in which  $R^7$  and  $R^8$  may be identical or different and are hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl,  $R^9$  is  $C_1$ - $C_4$ -hydroxyalkyl or a radical of the general formula IV



(IV)

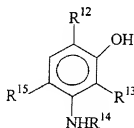
in which  $R^7$  and  $R^8$  are as defined above and  $m$  is an integer from 1 to 4,  $R^{10}$  is hydrogen or a radical of the general formula V



(V)

in which  $R^7$  and  $R^8$  are as defined above and  $n$  is an integer from 1 to 4,  
 $R^{11}$  is hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl,

(b) m-aminophenol derivatives

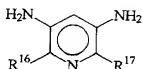


(VI)

in which  $R^{12}$  is hydrogen or  $C_1$ - $C_4$ -alkyl,  
 $R^{13}$  is hydrogen, fluorine, chlorine,  $OCH_3$  or  $C_1$ - $C_4$ -alkyl,  
 $R^{14}$  is hydrogen,  $C_1$ - $C_4$ -alkyl,  $C_1$ - $C_4$ -hydroxyalkyl or  $OCF_3$ ,  
 $R^{15}$  is hydrogen, fluorine, chlorine or  $OCH_3$ ,

with the provisos that  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  are not hydrogen at the same time and that, if  $R^{12}$  is methyl,  $R^{13}$ ,  $R^{14}$  and  $R^{15}$  are not hydrogen at the same time,

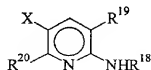
(c) pyridine derivatives of the formulae VII and VIII



(VII)

in which  $R^{16}$  and  $R^{17}$  may be identical or different and are fluorine, chlorine or  $OCH_3$ ,

5



(VIII)

in which  $R^{18}$  is hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl,

10

$R^{19}$  is  $OH$  or  $NH_2$ ,

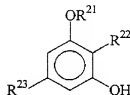
$R^{20}$  is hydrogen,  $C_1$ - $C_4$ -alkoxy or  $NH_2$ ,

$X$  is hydrogen or  $OCH_3$ ,

with the provisos that, if  $R^{19}$  is  $NH_2$ ,  $R^{18}$  and  $R^{20}$  are not  $C_1$ - $C_4$ -alkyl or methoxy respectively at the same time, and if  $R^{18}$  is hydrogen,  $R^{19}$  and  $R^{20}$  are not  $OH$  or hydrogen respectively at the same time,

15

(d) resorcinol derivatives of the formula IX



(IX)

20

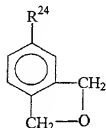
in which  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  may be identical or different and are hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl,

25

with the provisos that  $R^{21}$ ,  $R^{22}$  and  $R^{23}$  are not hydrogen at the same time, if  $R^{21}$  and  $R^{23}$  are hydrogen,  $R^{22}$  is not methyl, and if  $R^{21}$  is methyl,  $R^{22}$  and  $R^{23}$  are not hydrogen at the same time,



- (e) methylenedioxybenzene derivatives of the formula X



(X)

5

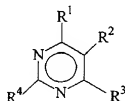
in which  $R^{24}$  is OH,  $NH_2$  or  $NHR^{25}$ , in which  $R^{25}$  is  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl, and

10

(f) 3,4-diaminobenzoic acid,  
for dyeing keratin fibers.

15

13. A method of dyeing keratin fibers, in particular human hair, in which a dyeing agent comprising  
A) at least one pyrimidine derivative of the general formula I



(I)

20

in which  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  may be identical or different and are hydrogen, OH,  $NH_2$  or a group  $NR^5R^6$ , in which  $R^5$  and  $R^6$  may be identical or different and are  $C_1$ - $C_4$ -alkyl,  $C_1$ - $C_4$ -hydroxyalkyl having a primary and/or secondary hydroxyl group,

25

where two of the radicals  $R^1$ ,  $R^2$ ,  $R^3$  or  $R^4$  together can form an optionally substituted 5- and 6-membered

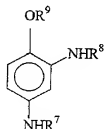
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heterocycle containing one or two nitrogen and/or oxygen atom(s) in the molecule,

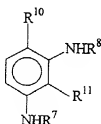
with the proviso that at least two of the radicals  $R^1$ ,  $R^2$ ,  $R^3$  or  $R^4$  are a group  $NH_2$  and/or  $NR^5R^6$ ,

B) at least one compound chosen from the group consisting of

(a) m-phenylene derivatives of the formulae II and III



(II)

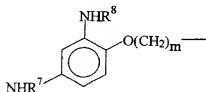


(III)

in which

$R^7$  and  $R^8$  may be identical or different and are hydrogen,  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl,

$R^9$  is  $C_1$ - $C_4$ -hydroxyalkyl or a radical of the general formula IV

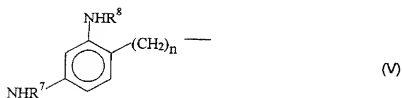


(IV)

in which

$R^7$  and  $R^8$  are as defined above and  $m$  is an integer from 1 to 4,

$R^{10}$  is hydrogen or a radical of the general formula V

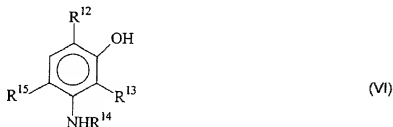


in which

$\text{R}^7$  and  $\text{R}^8$  are as defined above and  $n$  is an integer from 1 to 4,

$\text{R}^{11}$  is hydrogen,  $\text{C}_1$ - $\text{C}_4$ -alkyl or  $\text{C}_1$ - $\text{C}_4$ -hydroxyalkyl,

(b) m-aminophenol derivatives



in which

$\text{R}^{12}$  is hydrogen or  $\text{C}_1$ - $\text{C}_4$ -alkyl,

$\text{R}^{13}$  is hydrogen, fluorine, chlorine,  $\text{OCH}_3$  or  $\text{C}_1$ - $\text{C}_4$ -alkyl,

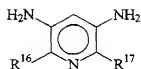
$\text{R}^{14}$  is hydrogen,  $\text{C}_1$ - $\text{C}_4$ -alkyl,  $\text{C}_1$ - $\text{C}_4$ -hydroxyalkyl or  $\text{OCF}_3$ ,

$\text{R}^{15}$  is hydrogen, fluorine, chlorine or  $\text{OCH}_3$ ,

with the provisos that  $\text{R}^{12}$ ,  $\text{R}^{13}$ ,  $\text{R}^{14}$  and  $\text{R}^{15}$  are not hydrogen at the same time and that, if  $\text{R}^{12}$  is methyl,  $\text{R}^{13}$ ,  $\text{R}^{14}$  and  $\text{R}^{15}$  are not hydrogen at the same time,

(c) pyridine derivatives of the formulae VII and VIII

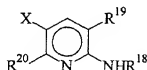
09669174-103104



(VII)

in which

R<sup>16</sup> and R<sup>17</sup> may be identical or different and are fluorine, chlorine or -OCH<sub>3</sub>,



(VIII)

in which R<sup>18</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkyl or C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl,

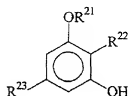
R<sup>19</sup> is OH or NH<sub>2</sub>,

R<sup>20</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkoxy or NH<sub>2</sub>,

X is hydrogen or OCH<sub>3</sub>,

with the provisos that, if R<sup>19</sup> is NH<sub>2</sub>, R<sup>18</sup> and R<sup>20</sup> are not C<sub>1</sub>-C<sub>4</sub>-alkyl or methoxy respectively at the same time, and if R<sup>18</sup> is hydrogen, R<sup>19</sup> and R<sup>20</sup> are not OH or hydrogen respectively at the same time,

(d) resorcinol derivatives of the formula IX



(IX)

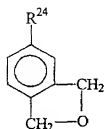
in which

R<sup>21</sup>, R<sup>22</sup> and R<sup>23</sup> may be identical or different and are hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkyl or C<sub>1</sub>-C<sub>4</sub>-hydroxyalkyl,

with the provisos that R<sup>21</sup>, R<sup>22</sup> and R<sup>23</sup> are not hydrogen at the same time, if R<sup>21</sup> and R<sup>23</sup> are

hydrogen,  $R^{22}$  is not methyl, and if  $R^{21}$  is methyl,  $R^{22}$  and  $R^{23}$  are not hydrogen at the same time,

(e) methylenedioxybenzene derivatives of the formula X



(X)

in which

$R^{24}$  is OH,  $NH_2$  or  $NHR^{25}$ , in which  $R^{25}$  is  $C_1$ - $C_4$ -alkyl or  $C_1$ - $C_4$ -hydroxyalkyl, and

(f) 3,4-diaminobenzoic acid, and customary cosmetic ingredients, is applied to the keratin fibers, left on the fibers for a while, usually about 30 minutes, and then rinsed out again or washed out using a shampoo.





## DECLARATION

Page 2

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365(d) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/EP99/09901	12/14/1999	

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☐ Firm Name  Customer Number  or label

☒ List Attorney(s) and/or agent(s) name and registration number below:

Name	Registration Number	Name	Registration Number
Wayne C. Jaeschke	21,062		
Glenn E. J. Murphy	33,539		
Stephen D. Harper	33,243		
Kimberly R. Hild	39,224		

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

Please direct all correspondence to:

☒ Customer Number  or label

00423

OR

☒ Fill in correspondence address below

Name	Kimberly R. Hild						
Address	Henkel Corporation						
Address	2500 Renaissance Blvd, Suite 200						
City	Gulph Mills	State	PA	Zip	19406		
Country	USA	Telephone	610-278-4964	Fax	610-278-6548		

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor:

☐ A petition has been filed for this unsigned inventor

Given Name	Horst	Middle Initial		Family Name	Hoefkes	Suffix e.g. Jr.	
Inventor's Signature					Date		
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Post Office Address							
City	40595 Duesseldorf	State		Zip		Country	Germany
						Applicant Authority	

☒ Additional inventors are being named on supplemental sheet(s) attached hereto



## DECLARATION

Page 2

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Address	2500 Renaissance Blvd, Suite 200						
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Country	USA	Telephone	610-278-4964	Fax	610-278-6548		

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## Name of Sole or First Inventor:

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Given Name	Horst	Middle Initial		Family Name	Hoefkes	Suffix e.g. Jr.	
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						Applicant Authority	

☒ Additional inventors are being named on supplemental sheet(s) attached hereto

**DECLARATION**
**ADDITIONAL INVENTOR(S)  
Supplemental Sheet**
**Name of Additional Joint Inventor, if any:**
☐

A petition has been filed for this unsigned inventor

Given Name	<b>Doris</b>	Middle Initial		Family Name	<b>Oberkobusch</b>	Suffix e.g. Jr.	
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Inventor's Signature	<i>Doris Oberkobusch</i>	Date	<i>August 1, 2001</i>
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Residence: City	<b>Duesseldorf</b>	State		Country	<b>Germany</b>	Citizenship	<b>Germany</b>
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Post Office Address	
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**Name of Additional Joint Inventor, if any:**
☐

A petition has been filed for this unsigned inventor

Given Name	<b>David</b>	Middle Initial		Family Name	<b>Rose</b>	Suffix e.g. Jr.	
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Inventor's Signature		Date	
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Residence: City	<b>Hilden</b>	State		Country	<b>Germany</b>	Citizenship	<b>Great Britain</b>
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Post Office Address	<b>Am Eichelkamp 223</b>
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Post Office Address	
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City	<b>40723 Hilden</b>	State		Zip		Country	<b>Germany</b>	Applicant Authority	
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**Name of Additional Joint Inventor, if any:**
☐

A petition has been filed for this unsigned inventor

Given Name	<b>Melanie</b>	Middle Initial		Family Name	<b>Hitz</b>	Suffix e.g. Jr.	
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Inventor's Signature	<i>Melanie Hitz</i>	Date	<i>August 1, 2001</i>
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Residence: City	<b>Dormagen</b>	State		Country	<b>Germany</b>	Citizenship	<b>Germany</b>
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Post Office Address	
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City	<b>41542 Dormagen</b>	State		Zip		Country	<b>Germany</b>	Applicant Authority	
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**Name of Additional Joint Inventor, if any:**
☐

A petition has been filed for this unsigned inventor

Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
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Inventor's Signature		Date	
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Residence: City		State		Country		Citizenship	
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Post Office Address	
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Post Office Address	
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City		State		Zip		Country		Applicant Authority	
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☐ Additional inventors are being named on supplemental sheet(s) attached hereto

DECLARATION				ADDITIONAL INVENTOR(S) Supplemental Sheet			
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name	Doris	Middle Initial		Family Name	Oberkobusch	Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City	Duesseldorf	State		Country	Germany	Citizenship	Germany
Post Office Address	Auf'm Rott 81						
Post Office Address							
City	40591 Duesseldorf	State		Zip		Country	Germany
						Applicant Authority	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name	David	Middle Initial		Family Name	Rose	Suffix e.g. Jr.	
Inventor's Signature	David Rose				Date	August 1, 2001	
Residence: City	Hilden	State		Country	Germany	Citizenship	Great Britain
Post Office Address	Am Eichelkamp 223						
Post Office Address							
City	40723 Hilden	State		Zip		Country	Germany
						Applicant Authority	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name	Melanie	Middle Initial		Family Name	Hitz	Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City	Dormagen	State		Country	Germany	Citizenship	Germany
Post Office Address	Platanenstr. 10						
Post Office Address							
City	41542 Dormagen	State		Zip		Country	Germany
						Applicant Authority	
Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country	
						Applicant Authority	
<input type="checkbox"/> Additional inventors are being named on supplemental sheet(s) attached hereto							